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(f) Int. CLS, A61L 29/00, A61L 33/00

A request for addition of the description has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO. A-V.

Priority: 30.09.92 US 954906

Date of publication of application: 20.04.94 Bulletin 94/16 **②**

Designated Contracting States: BE DE ES FR GB NL 3

730 Central Avenue Murray Hill New Jersey 07974(US)

stretching and expansion. The coated products produced by this process have an uniformly functional tional agent (e.g., poly(ethylene oxide), a hydrophilic polyurethane or polysiloxane) dispersed, or emulsilied in a carrier such as water and/or an organic solvent. Conventional fabricating procedures are used for stretching and expanding the coated tubing. Optional steps may include a heating step during (9) A process for preparing expanded thermoplastic medical products (e.g., dilatation balloons) having coatings or protective coatings is disclosed. The process involves the steps of coaling a suitable expandable thermoplastic tubing with the blomedical functional coaling, at least partially drying the coated tubing, and then stretching and expanding the coated tubing. The coating comprises at least one funcbiomedical functional coatings such as lubricous FP 0 592 870 AT

(i) Applicant: C.R. BARD, INC.

Inventor: Tedeschi, Eugene Inventor: Elton, Richard K. Still River, Mass.(US) 8 Wing Street Glens Falls, N.Y.(US) 216 Still River Road **(2)**

Representative: Laufhütte, Dieter, Dr.-Ing. et al Lorenz-Seldier-Gossel Widenmayerstrasse 23 D-80538 München (DE) **②**

Process for preparing functionally coated expanded products from expandable tubing and the expanded products produced thereby.

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BACKGROUND OF THE INVENTION

tic medical products, particularly to a novel process for preparing an expanded thermoplastic medical hered to the expanded surface, particularly coated product having a functional biomedical coaling ad-This invention relates to expanded thermoplasballoons for use on calhelers.

at Col. 4, lines 48-54 and exemplified at Col. 5, lines 41-44 of U.S. 5,026,607 (ssued June 25, 1991 to M. Klezulas). The dilatation balloons are bonded to an appropriate catheter shaft using an by dipping or spraying. The coated surface is allowed to dry and cured if necessary. coatings to balloons utilizes the step of applying the coating to the pre-formed balloon, i.e., to the blow molded balloon. Preferably the coating is applied to the inflated pre-formed balloon. Applying tion of a coating layer having a generally uniform thickness. A typical coating procedure is described first formed from the appropriate tubing by a series of stretching, optionally heating, and expanding operations such as blow molding. Then the balloon is adhesive or other appropriate means. Alternatively the tubing may be an integral part of the catheter. Finally, the functional coatings are applied, typically the coating to the inflated balloon allows the forma-The prior art process for applying functional

vents tend to permeate the thin wall of the balloon and atter the physical properties, e.g., by changing Current functional coatings used on pre-formed balloons are generally limited to water borns dispersions and emulsions because most organic solthe polymer crystallinity.

There are several disadvantages to coating processes which involve applying the functional coating to a pre-formed balloon. These disadvantages include the following:

objects can be inconsistent due to non-uniform drainage of the coating solution as it flows off (i) the coating thicknesses on irregularly shaped the coated object, and some balloon geometries may promote entrapment of air during coaling. thus producing a product with cosmetic irregularities;

sensitive to any heating operations that may be 50 required for curing a coating or driving off solcrystalline and thus are very sensitive to changes caused by contact with the solvents present in some coaling solutions; and are also (ii) pre-formed balloons are highly oriented and

(iii) to minimize the effect of solvent exposure on apply the coating by spraying rather than dip-ping, in which case there are safety concerns with flaamability, exposure to the finely divided solvent mist, and unwanted side effects on the pre-formed balloons it may be necessary to

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coating due to evaporative cooting of the finely divided droplets formed during spraying; and (iv) the high value loss of coated pre-formed balloons and coated finished catheters which are caused by coating errors.

SUMMARY OF THE INVENTION

expandable thermoplastic tubing material suitable for a medical product with a coating containing a functional biomedical material and a carrier and to It is an object of the invention to coat an then expand the coated tubing to form an expanded medical product with an adherent coating of the functional biomedical material. 2

It is also an object of this invention to coat an expandable thermoplastic tubing suitable for forcoated tubing to form an expanded balloon with a uniformly functional, highly adherent coating on its ming a balloon with a coating which contains a functional blomedical material and to expand the outer surface.

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It is a further object of the invention to coat an expandable thermoplastic tubing suitable for blow ing and to blow mold the coated tubing to form a molding a dilatation balloon with a fubricious coatjubrictous dilatation balloon.

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(a) applying to at least a portion of an inner and/or an outer surface of an expandable thermoplastic tubing at least one adherent functional biomedical coating which comprises at least one The present invention provides a process for preparing a coated expanded thermoplastic medical product. The process comprises the steps of:

(b) allowing the coated tubing to dry at a time and temperature sufficient to remove at least part of the carrier; and functional agent and a carrier;

(c) stretching and/or expanding the dried coated tubing with an inflating fluid at a pressure sufficient to form the functionally coated expanded medical product. The expanded thermoplastic medical products prepared by this process are unitormly functionally coated.

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The present invention provides a process for preparing a coated balloon. The process comprises

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(a) applying to at least a portion of an inner and/or an outer surface of an expandable thermoplastic tubing at least one adherent functional biomedical coaling which comprises at least one

(b) allowing the coaled tubing to dry at a time and temperature sufficient to remove at least was to the coale of the coal functional agent and a carrier;

(c) stretching and/or expanding the dried coated tubing with an inflating fluid et a pressure suffi-cient to form the functionally coated balloon. part of the carrier; and

The present invention also provides a process preparing a lubricious dilatation balloon. The

poly(ethylene oxide) dissolved, dispersed, or emulsified in the carrier, and (iii) a polymer selected from the group consisting of a polyurethane, a polyurea, and a polyurethane-urea or polymer precursors selected from the group consisting of polyurethane precursors and polyurea precursors, the polymer or polymer precursors being dissolved, dispersed, or emul-(a) applying to at least a portion of an outer surface of an expandable thermoplastic tubing at least one adherent functional biomedical coaling which comprises (i) one or more carriers. (ii) a process comprises the steps of:

and temperature sufficient to remove at least (b) allowing the coated tubing to dry at a time sified in the carrier(s):

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third in order to increase the diameter and length of the tubing while simultaneously orienting the tubing. The fubricious dilatation balloons prepared by this process are uniformly functionpart of the carrier; and (c) expanding the coated tubing with an inflating ally coated.

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As used herein, the term "thermoplastic" is exclusive of natural or synthetic rubbers. It is understood that thermoplastic materials which can be formed into a tube, coated, and then subjected to further heat treatment to cure the coating and/or the tubing and form a thermoset tube are also suitable for use herein.

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ments. The functional biomedical coatings useful herein must exhibit adhesion suitable for the intended end use of the medical product and they should have the potential for reasonably high radial ings are usually, but not necessarily activated in an ture resistance and/or tear resistance, (ii) functional properties such as lubricity, thromoboresistance, hemocompatibility, and (iii) therapeutic properties such as anti-thrombogenic properties, antimicrobial As used herein, the term "functional biomedical coating" is used for coatings applied to medical products intended for use in the body. Such coataqueous environment, and they provide (i) protective properties such as abrasion resistance, puncproperties and the like, and like functional improveand circumferential stretching.

The carriers used for the coalings can be either an organic solvent or water, with the choice depending on the coating components and on the some cases one or more organic solvents may be used, whereas in other cases water may be used as the carrier. Suitable solvents are those which do 1000

methylene chloride methylene bromide, trich-loroethylene, ethylene dichloride; and mixtures of the above. The chlorined solvents are particularly as ethylene glycol methyl ether; esters such as methylpyrrolidone, and pyridine; nitroparaffins such as 2-nitropropane; chlorinated solvents such as which are used to form the linal expanded product from the coated tubing. Suitable solvents include alcohols such as ethanol or ethylene glycol: ketones such as methyl ethyl ketone; elhers such col monoethyl ether acetate; aromatic and aliphatic solvents such as benzene, toluene, xylene, Nethyl acetate: ether acetates such as ethylene glyuseful for poly(ethylene oxide) containing coatings.

even after the radial and circumferential stretching of several hundred percent which is involved in The ability to maintain a continuous coating over the surface of the thus-expanded balloon.

Applying the functional biomedical coating to

(i) it is possible to coal the tubing using solvents which would otherwise attack and deform a preformed polymeric material such as a dilatation balloon, thus greatly broadening the range of

(ii) It is much less expensive to discard rejected coated tubing than to discard rejected coated pre-formed objects such as catheler balloons or assembled cathelers with attached balloons:

er than a pre-formed object, such as a balloon, with a potentially complex geometry:

unilke pre-formed expanded products such as (iv) it is possible to readily cure coatings requiring elevated temperatures because the tubing. dilatation balloons or assembled products, can tolerate the significantly higher temperatures required to cure many coating compositions;

nents of a multi-component device lends itself to (vi) separately coating the individual compomulti-component device; and

expanding the balloon, is highly advantageous.

the expandable thermoplastic tubing prior to expansion provides the following advantages:

coatings which can be used;

(iii) it is much easier to control the uniformity of the resulting coating because the material being coated, i.e., the tubing is a simple cylinder rath(v) separately coating the components of a multi-component device allows one to produce a device with different performance properties for each component, depending upon the coating on each component, and this cannot be obtained if one is limited to coating the entire

more efficient production because it allows standard mullaneous manufacturing steps to occur in parallel rather than in series.

on factors such as the function desired (i.e., fubricity, hemocompatibility, antimicrobial properties, etc.), the ability of a particular coating to bond to the thermoplastic tubing material, the ability of the coating to endure the stretching and/or expanding process, durability (e.g. abrasion resistance) required of the coating in its intended application. and the like. One skilled in the art of coating will weigh these factors in making an appropriate Similarly, there is a wide range of functional biomedical coatings which can be adapted for use in this process. The choice of coating will depend 0

desirable because poly(ethylene oxide) has the desired functional characteristic of "passivating" a bogenic. See Chapter 4 "Poly(ethylene oxide) and 113) in "Hydrogels in Medicine and Pharmacy". Vol. II Polymers, ed. by N. A. Peppas, CRC Press, Inc., Boca Raton, Florida, 1986. Coatings containing poly(ethylene oxide) are surface toward platelets and it is quite non-throm-Related Hydrogels" by Nell B. Graham (pp. 95-

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when complexed with a complexing polymer, a high degree of durability. These properties are Such coatings provide a combination of useful properties, namely, lubricity, biocompatibility and, particularly useful and sought after in dilatation balloons.

oxide) and polyurea precursors . Preferred coatings contain poly(ethylene oxide) blended with polyurepolyureas, or polyurethaneureas are particularly thane precursors which are polymerized and crossinked in situ on the coated surface. (ethylene oxide) and pre-formed polyurethanes. useful, as are coatings containing poly(ethylene Functional biomedical coatings containing poly-8 32

are coatings of the type described in <u>U.S.</u> 5,077,352 (issued December 31, 1991 to R. K. Eiton), the disclosure of which is incorporated herein by reference. These coatings are applied as a solution of an isocyanate, a polyol, and a high Particularly preferred for applications requiring sistance and a high poly(ethylene oxide) content molecular weight poly(ethylene oxide).
After application of the coaling, at least a porpermanent lubricity, coating durability, abrasion re-

ably, the weight ratio of isocyanate and polyoi to polyletrylene-oxide) varies from 0.25-10-6.0 and most preferably from 0.75-16-2.0. The stoichiometric ratio of total NCO groups in the isocyanate to total OH groups in the polyol may vary from 0.8 to 3.5, preferably from 0.85 to 1.5. Advantageously, when used as the coating in the cured by allowing the polyol and isocyanate to thane matrix associated or complexed with the tion of the solvent is removed and the coating is react to form a crosslinked substantially polyurepoly(ethylene, oxide), by, hydrogen bonding. Prefer-

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DESCRIPTION OF THE PREFERRED EMBODI-MENTS

2 copolymers: ethylene-virtyl acetate copolymers: polyether polyamide block copolymers such as Pelaxée: volycarbonates; ionomers such as Suromatic polyamides; polyetherimides; polyamideimides; and the like. One skilled in the performance parameters required for the balloon, coating adhesion, and biocompatibility in making The expandable thermoplastic tubings to be coated include tubings made from the materials typically used to form expanded products such as propylene, polyethylene terephthalate or block copolymers thereof admixed with low molecular similar compositions employing butadiene or isoprene in place of the ethylene and butylene; polylyne; polybutylene terephthalate, polyarylather ketones; polyimides: polyamides particularly arart will consider such factors as processability. dilatetion belicons, esophageal dilatation balloons, fallopian tube dilatation balloons, peripheral angloplasty dilatation balloons, prostate dilatation balloons nipulator balloons and the like, included among the suitable thermoplastic materials are polyurethanes, weight styrene and optionally polypropylene, and vinyl chloride; copolyesters; silicone polycarbonate loons, coronary angioplasty balloons, uterine mapolyethylene, ethylene-butylene-styrene. poly-

the appropriate selection.

The choice of dilatation balloon material will depend on the particular application. For example, depend on the particular application. For example, some applications will require a rigid non-compliant some applications will require a rigid non-compliant. polymer, while other applications will favor the use of a softer polymer.

of the balloon as well as its elasticity. If the segmented polyurethane to be coated is a hard polyment then preferably a hard polymer should be used in the functional coaling. If the segmented preferably a softer polymer should be used in the functional coating. Of particular interest for dilatapolyurethane to be coated is a soft polymer, then tion balloons are certain PELLETHANE® polyure-Segmented polyurethanes can be varied by using different Isocyanates and polyols and different ratos of hard to soft segments in the polymer. The hard to soft ratio defines the expansion capabilities Segmented polyurethanes are suitable as thermoplastic tubing materials for ditatation balloons. hane polymers (e.g., PELLETHANE® 2367-75D).

ene terephthalates (PET), particularly high, molecus-lar weight homoplymers of 'PET and PET copolyesters. Balloons made from PET tend to be ss highly rigid when inflated and are capable of sustaining high inflation pressures even when the bal--ing-materials for dilatation_balloons_are_polyethylioon wall thickness is thin, e.g., less than 0.002".

patent is prepared by weighing appropriate quantities of isocyanate, polyol, and poly(ethylene oxide), adding them to an appropriate solvent, and adding additional solvent as needed to adjust the solids content to the desired level. Suitable organic aby halogenated solvents such as methylene chlo-ride, methylene bromide, dichloroethane, dibromoethane, chloroform, and trichloroethylene, and blends of the above. Solids contents in a range solvents for this coating may include acetonitrile, dioxolane, n-methyl pyrrolidone, pyridine, prefer-

of from 0.4 to 40% are preferred.
Another functional poly(elinylene oxide) coaling useful herein is the hydrophilic coaling described in U.S. 4.459.317 (Issued July 10, 1984 to H.R. Lambert), the disclosure of which is incorporated herein by reference. A first coaling of unreacted iscoyanate groups on the polymer surface is formed by applying a solution containing a comformed by applying a solution containing a compound having at least two unreacted isocyanate groups per molecule and then evaporating the solvent by air drying. A second coating of poly- (ethylene oxide) dissolved in a solvent is then applied, the solvent is evaporated off. and finally (ethylene exide) - polyurea interpolymer formed when the isocyanate groups react with water during the curing to yield an amine which rapidly reacts with other isocyanate groups to form urea cros-50-100°C in the presence of a water-containing gas such as ambient air. Known isocyanate curing catalysts may be added to one or both coaling solutions. The coating normally consists of a polycoating is cured, preferably for 5-30 minutes at

Suitable isocyanates include polymethylene polyphenyl isocyanate, 4.4'-diphenylmethane diisocyanate, and 2.4-toluene diisocyanate, as well as prepolymers or other addition products of Isocyanates and polyots. Suitable solvents for tho isocyanate compound are ethyl acetale, acelone, chloroform, methyl ethyl ketone, ethylene dichloride, and preferably methylene chloride. The isocyanate solution may contain 0.5 to 10%, preferably 1 to 6% (weight/volume), of the isocyanate

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The poly(ethylene oxide) used should have a preferably 105. A suitable poly(eithylene oxide) is poly(ethylene oxide) are the same as those under the trade name Polyox® by Union Carbide Corp. The preferred and suitable solvents for mean molecular weight of between 10° and 107.

discussed above. The proportion of poly(ethylene oxide) is preferably between 0.5 and 10%, most preferably between 2 and 8% (weight/volume).

(ethylene oxide) coalings are found in U.S. 4.990.357 (issued Feb. 5, 1991 to M. Karakelle et al.). Of the several functional coatings disclosed in the '357 patent, the coatings containing poly-(ethylene oxide) are useful herein for coating the thermoplastic tubing used to form dilatation bal-loons. Suitable coalings are uniform blends of an elastomeric segmented hydrophilic poly(urethanes) (HPEU) and poly(elthylene oxide) in an aqueous liquid. The poly(elthylene oxide) should be present Examples of other useful functional polyin an amount of about 5 to 25 wt. %.

polytither glycol, and a chain extender. Suitable disocyanates are aromatic disocyanates such as insurance and disocyanates are aromatic disocyanates such as isophorone disocyanate and disocyanates such as stophorone disocyanate and 4,4-dicyclohoxylmethane disocyanate, and alphatic disocyanates, such as haxamathylene disocyanate. The most preferred disocyanate is MDI. The polyether glycol component may be polyethylene glycol (PEG), alone or mixed with polypropylene oxide glycol or polylenameltylane oxide glycol. The preferred polyol is PEG having a moter preferred polyd is PEG having a most preferred polydener glycol is PEG having an everage molecular weight of from about 800 to 3300 or a mixture containing at least 50 vt. % thereof. The most preferred polydener glycol is a PEG having an everage molecular weight of 1000 to 1450. The chain extender may be water and/or a low molecular weight of most preferred or unbranched diol, diamine or mixture or mixtu amino alcohol of up to 10 carbon atoms or mix-tures thereof. The polymer thus formed is prepared without the use of a catalyst and the resulting product is a polyurethane or a polyurethaneurea The HPEU is prepared from a disocyanate, a depending upon the chain extender used. 2 33 8

Additional examples of useful functional poly-(ethylene oxide) coalings are found in U.S. 5.041,100 (issued August 20, 1891 to S.M. Row-land et al.), the disclosure of which is incorporated herein by reference. Of the poly(ethylene oxide) coatings disclosed in the Rowland et al. palent, coalings where the structural plastic is a thermo-plastic, solvent-soluble linear polyurethane are use-ful for coating the thermoglastic tubing used for of the polyurethane and 2 to 50 wt. % of a poly-(ethylene oxide) having a molecular weight of at least 10,000, preferably at least 1,000,000: Coat-ings which contain 10% to 30% poly(ethylene.oxide) are most useful herein. Typically, an aqueousforming dilatation balloons. These coatings comprise an intimate physical mixture of 50 to 98 wt. % oxide) is used. There is no need for any curing step to effect cross-linking. The coatings provide at dispersion of the polyurethane and poly(ethytene east temporary lubricity and may be benefictally

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employed in applications where temporary lubricity is sufficient or even desirable.

Takenura et al. 11th God Unyungunden polyunethane polyusatar restins having free hydroxyl groups and carboxylate groups in the polymer backbone. The functional profective fubrications of the polymer backbone. The functional profective fubrications are accordance to the series of th Quount, ponywing nacuous access acces Other functional lubricious coatings useful herein include hydrophilic polyurethanes such as those disclosed in U.S. 4,156,066 and U.S. 4,156,067 (both issued May 22, 1979 to F.E. Gould); polyvinyl alcohols such as those disclosed

pected that such coalings will be useful herein provided the PVP is adequately modified to accept the conditions of the expansion slep, for example. Incorporated herein by reference.

Many functional tubricious coating used in biomedical applications contain a significant amount of polyvinyl pyrrolidinone (PVP). It is examount of polyvinyl pyrrolidinone (PVP). It is examount of polyvinyl pyrrolidinone (PVP). hrough the use of plasticizers, PVP copolymers, or other PVP modifiers.

derstood that certain coaling additives commonly used in formulating coalings may be beneficially employed to produce a destrable result. Exemplary coating additives include surfactants or wetting agents, viscosity and flow control agents, antioxidants, pigments, and air release agents or defeats, For all functional blomedical coatings, it is un-

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Surfactants or wetting agents are used to promote wetting to the substrate as well as adhesion of the costing to the substrate. Useful wetting agents include perfluorcalkyl ethoxylate mixtures, 2,479-tetramethyl 1-5-Gecyn-4,7-diol and ethylene oxide adducts thereof, 2,3,5-dimethyl-1, hexyn-3-ol, condensation products of ethylene oxide and di-

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turned silica, collutose acetate butyrate and ethyl acrylate copolymer. Flow control agents are preferably used in amounts from 0.05 to 5 wt. % of coaling.
Antioxidants are used to improve the oxidative stability of the coalings and include but are not ing can be formed on the thermoplastic tubing at the desired thickness. Viscosities of from 50 cps to 500 cps can be used, although higher or lower viscosities may be useful in certain instances. Viscosity control agents include, but are not limited to.

buryphenyl) butane. Antioxidants are preterably used in amounts from 0.01 to 1 wt. % of coaling. Conventional pigments can be added to impart color or radiopacity or to increase the desired limited, to tris (3,5-di-1-butyl-4-hydroxybenzyl)-isocyanurate, 2,2-methylenebis(4-methyl-6-l-butyl phenol). 1,3,5-trimethyl-2,4,6-tris(3,5-di-butyl-4hydroxybenzyl) benzene. butyl hydroxy toluene. octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate. 4.4-methylenebis(2,6-di-t butylphenol), p.p.-dioctyl diphenylamine, 1,1,3-tris-(2-methyl-4-hydroxy-5-l-

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appearance of the coatings.

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Air release agents or detoamers are added to quickly release air bubbles formed in the wet film during the coating operation. They include, but are not limited, to polydimethyl siloxanes, 2.4.7.9 (etramethyl-5-decyn-4,7-dio), 2-ethylhexyl alcohol. 25

and n-beta-aminoetry-tgamma-amino-propyl-trimethoxysilane. Air release agents are often used in amounts from 0.005 to 0.5 vr. % of the coating. Additionally, the functional biomedical coatings

may also contain an effective amount of a therapeutic agent which can diffuse out of the coating in a continuous, controlled dosage over a substantial period of time.

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Specific examples of such therapeutic agents include anti-thrombogenic agents or other agents for suppressing acute thrombosis, stenosis or tate streptokinase, urokinase, tissue plasminogen activator, anti-thromboxane B₂ agents, anti-B-thromboglobulin, prostaglandin E, aspirin, dipyridamole, anti-thromboxane A₂ agents, murine monoclonal antibody 7E3, triazolopyrimidine, ciprostene, hirudin, ticlopidine, nicorandil, and the like. Antiplatelet derived growth factor may be used as a therapeutic agent to suppress subinitimal fibromuscular hyperplasia at an arterial stenosis restenosis in arteries. Such agents include heparin, site, or any other inhibitor of cell growth at the stenosis site may be used.

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The therapeutic agent also may comprise a vasodilator to countered vasospasm, for example, an antispasmodic agent such as papaverine. The therapeutic agent may be vasoactive agent such as calcium antagonists, or alpha and beta adrenergic

agent may comprise steroids for the purpose of The therapeutic agent may be an antibiotic which may be applied, optionally in conjunction with a controlled release carrier for persistence, to an infected stent or any other source of localized infection within the body. Similarly, the therapeutic suppressing inflammation in a localized tissue site.

Also, anti-infective agents such as chlorhexidine may be added for improved infection resis-

tance of the coated product.

ternary ammonium compounds and/or amino-functional poly(ethylene oxide) to modify the release kinetics of therapeutic agents carried in the coaling. The coating may contain binders such as qua-

The above functional biomedical coalings are typically applied using conventional methods. One and of the tubing is sealed and the outer surface of ping, spraying, wiping, painting or the like. Preferaby, the tubing is dipped at about 20-25 °C and less than 60% relative humidity. Coating thickness and functionality can be affected by withdrawal rate the tubing is coated using a method such as dip-Care should be taken in adding other agents to the coating mixture. The agents should be compatibie with the functional agent and the agents used should not adversely affect each other's properties.

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minutes, or the tubing is dried at temperatures of 10 to 205°C from for from a few seconds to 48 hours. The time and temperature selected witl, of course, depend upon the carrier used and the speed with which evaporation is desired. In all Atter applying the coating, the carrier is allowed to evaporate from the coated thermoplastic tubing, often by exposure to ambient conditions for a suitable drying time, typically from 15 to 480 cases the drying conditions should be non-deleterious to the underlying thermoplastic tubing. of the tubing from the coating mixture.

stretching and expanding steps used in blow molding. One skilled in the art will select the proper The coated thermoplastic tubing is fabricated moplastic tubing coated and the type of functional coating applied. In most cases, the stretched tubinto an expanded product using the conventional conditions, which will depend on the type of thering is heated during stretching and expansion.

suitable temperature a polymeric tubing having a finite length (L.) and an internal diameter (ID.) to a '983 patent is carried out by drawing at a length (L2) which is 3 to 6 L1, then expanding the When a coated dilatation balloon is being pre-And the second of the second

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lubing during the expansion step. If the tubing extends beyond the mold, the use of a restraining means is preferred to maintain the dimensions of ture. A suitable temperature is one within the range extending from the second order transition temperature to the first order transition temperature to Similar temperatures can be used for both the drawing and expanding steps. The desired temperature can be achieved by any suitable heat generating means. For polyethylene terephthalate (PET) the preferred temperature is 84-89 °C. For polyurethanes the temperature will vary depending upon the polyurethane's composition and the detemperature. The process can be carried out in conventional equipment. A mold having a cavity with dimensions commensurate with the desired a suitable fitting so that a pressurized fluid (e.g., a gas such as nitrogen) can be introduced into the pressure is being applied to the inside wall of the tubing. After the drawn tubing is positioned in the thermoplastic polymer used for the tubing. 10, followed by cooling the drawn and expanded tubing to less than the second order transition used. The open end of the tubing is equipped with the tubing in the region outside the mold while the mold, heat is applied to raise the tubing's temperadrawn tubing of internal diameter (ID1) which is 6-8 of the balloon to be produced is typically sired characteristic of the final product. 휼

tube drawing step is typically performed prior to the tube expansion step, the latter can be per-formed immediately after the drawing of the tubing. It will understood by one skilled in the art that some adjustments in the drawing and expansion ratios and in the drawing and expansion temperalures may be necessary to fabricate balloons. One skilled in the art will recognize that, although the or it can be performed at a later time.

shaped polymeric structures which are drawn by the above procedures, it may be necessary to maintain axial tension on the drawn tubing during the above procedures, it may be the expansion step.

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The coated balloons are attached to the catheters using conventional methods such as crosslinking adhesives, hot melt adhesives, plastic welding. or the like. Typically, the catheters are not coated.

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al.). The assembly is formed of two heat-shrinkable. The present process can be used to coal the tube being coaxially disposed within the second tube in such a manner that the second tube sur-rounds the first tube. Near the distal end of the Inflatable annular portion of Integral dilatation catheters such as the combination guiding catheterditating catheter assembly described in U.S. 4,323,071 (issued April 6, 1982 to J.B. Simpson et

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heated along its length in a suitable manner, such as by a hot air tool to a suitable temperature of about 120°. The second tube shrinks and forms a tight seal with respect to the first tube. Alternative methods for forming the catheter are disclosed in nutar portion to permit the introduction of an expansion fluid into the balloon-like portion for inflating the '071 patent, the disclosure of which is incorporated herein by reference. Alternatively, the entire second tube of the combination can be coated instead of just the balloon. Any of the above functional biomedical coatings can be used and the balloon can then be inflated in the conventional between the second tube and extends from the proximal end into the balloon-like or inflatable anthe balloon-like portion and for withdrawing the expansion fluid to deliate the balloon-like portion. The second tubular member is then progressively annular portion. An annular Ilow passage is formed

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illustrative and that other embodiments and modifications may be apparent to those skilled in the art should be understood that the foregoing description of the invention is intended merely to be without departing from the spirit of the invention.

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Example 1

a. Preparation of Premix

solution was not uniform (i.e., if any lumps or gels were present), the lumps or gels were broken up and the solution was allowed to stand for 24 hours. The solution was then rolled for about 60 minutes of methylene chloride about 132 g. of a poly-(ethylene oxide) marketed under the trade name chloride was prepared by adding to about 3868 g. POLYOX® WSR N-750 NF reshr: The POLYOX® Registry No. 25372-68-3) with an approximate molecular weight of 300,000. The mixture was rolled at 6-10 rpm for at least 24 hours. If the resulting A poly(ethylene oxide) premix in methylene WSR N-750 NF resin is a water-soluble resin (CAS to form a uniform solution of 3.3 wt. % total solids.

b. Preparation of Coating

from the Coatings Division of miles Corp. metrous distortion lemperature. D-1044 for Taber abrasion. The final coating was prepared by adding a polyester polyol and an aromatic poly(isocyanate) mPa's. Typically, the colorless to light yellow liquid has a OH content of 1.8%, average equivalent tent of 0.10 wt. % maximum, Gardner color of No. 2 maximum, and viscosity at 73°C of 900-1600 to the poly(ethylene oxide) premix. The polyester from the Coatings Division of Miles Corp. Multron polyol used was. Multron. R.18. which is available

weight of 935, specific gravity of 1.19 @ 5°C, weight per gallon of 9.9 lbs., viscosity @ 20°C of 26,000 mPa's, and flash point (Pensky-Marten closed cup) of 204°C (400°F). The isocyanate used was Mondur CB-60 which is evallable from the Coatings Division of Miles Corp. Mondur CB-60 is an aromatic polyisocyanate adduct based on NCO content of 10.0 - 10.8%, Gardner color of No. 4 maximum, viscosity @ 20 · C of 150-600 mPa's. and free TDI monomer content of 0.7% maximum. Typically, the clear, slightly yellow liquid has an @ 25 C of 1.13, weight of 9.4 lbs. per gallon, and (25:15), it has a solids content of 60 \pm 2 Mt. %, equivalent average weight of 404, specific gravity toluene diisocyanate (TDI) dissolved in propytene glycol monomethyl ether acetate (PMA) and xylene flash point of 28 °C (82 °F).

A total of 6.72 g. of the polyester polyol was added to an appropriately sized container. Then 3.22 g. of the isocyanate were added, followed by 265.3 g. of the poly(ethylene oxide) premix and then by 421.7 g of methylene chloride. The resulting mixture was mixed on a roller for at least 5 minutes and until it was visually homogenous. The coating solution had a total solids content of about

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c. Application of the Coating

weight, 1000 cycles) of SS mg. loss; Clash-Berg Modulus (Ti) of +9 °C; and flexural modulus ~ 190,000 ps; The ASTM test metriodS used are as fortows: D-i238 for metl Index; D-2240 for hardand outer dimensions ranging from 0.0151 to 0.0476 were heat sealed at one end. The tubing used was PELLETHANE® 2363-75D available from Dow Chemical Co. PELLETHANE® 2363-75D is a about 34 gm/10 min. (224°C. 5000 g.); Durometer D hardness of 74, ±, 4; specific gravity of 1.21; tensile modulus of 165,000 ps; utilimate tensile strength of 6960 ps; utilimate elongation of 250%; tear strength (Die C) of 14 pli; heat distortation temperatures of 65 and 55 at 66 and 264 psi. Thermoplastic polyurethane tubings having inner diameters ranging from 0.0077 to 0.0238 inwell thicknesses ranging from 0.0037 to 0.0119 inwell thicknesses ranging from 0.0037 to 0.0119 in. polyether polyurethane resin used for extrusion and injection molding. Typically, it has a melt index of respectively; Taber abrasion (H-22 wheel, 1000 g. ness; D-792 for specific gravity; D-412 for tensile modulus, ultimate tenule strength and ultimate elongation; D-624 for tear strength; D-648 for heat ŝ 35 \$ 9

The coating was applied by dipping the tubing in the above solution. The tubing was introduced at a rate of about 25 inches per minute and withdrawn

flexural modulus.

d. Evaluation of the Coating on the Tubing

The surface of the tubing contained a continuous coating of a crosslinked polyurethane complexed or associated with poly(ethylene oxide). When viewed under an optical microscope, the smooth coating was observed to be free from fissuring, crazing or other signs of coating rupture.

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mersed in the solution for approximately 30 seconds. The tubing was then held under running lap water to remove excess Congo Red solution. There was a marked line of distinction where the coated portion of the tube met the uncoated section, as demonstrated by the red color. The tubing was Coating continuity was evaluated using a 0.5% aqueous solution of Congo Red. The solution was poured into an appropriately sized and shaped cylinder. The coated tubing to be tested was Imthen viewed under 20X magnification. A continuous red film was observed.

firm pressure, and comparing the ease of move-ment to that observed when performing the same less on a similar wet tubing which had not been coated. The uncoated tubing, even when wet, of fered significantly more resistance to movement The wet coaling on the tubing exhibited a high degree of lubricity as determined by rubbing the coated tubing between the fingers while applying a than the coated tubing.

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The abrasion resistance of the coaling was determined by placing the coated, stained tubling under a stream of running tap water again so that the coating would be rabydrated. While under the running water, the tubing was rubbed between the finger and thumb for a total of 20 times while applying firm finger pressure. After this, the coaling still exhibited a continuous red color along the tubing, indicating that it did not wear off. Further examination for lubricity showed that the lubricity of the section of tubing given the above abrasion test was the same as a similar section that was not

The integrity of the coating after the abrasion test was further verified by altowing the coated tubing to dry and reexamining the coated surface under a 50 X optical microscope. A continuous,

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The coaled lubing was then subjected 10-10-cycles of wetting, lubricity testing, and drying. It was found that the lubricity did not change even

The tubricity was further tested by determining the coefficient of friction using a procedure based

on ASTM D-1894. In this test, five uncoated pieces of the thermoplastic tubing were affixed parellel to a stationary platform. The platform with the pieces attached was immersed in 38 °C water. A sted (200 gram stainless steel warpped in statex rubber) was attached to a load cell and transfer mechanism. neito; required to put the sted was recorded. The control tubings were replaced with the coated thermoplastic fubings, and the test was rerun. Once again, the force (both static and kinetic) required to put the sted was recorded. The coated tubos showed a consistent decrease in friction of approxi-The sled was placed on the samples and pulled across the surface of the tubing at a rate of six inches per minute. The force (both stalic and kinches mately 50%.

e. Formation of the Balloon

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Balloons were then formed as follows. The coated polyurethane tubings were placed in a mold which has a cavily with dimensions equivalent to the desired size of the balloon to be formed. The non-sealed end of the coated tubings were attached to a nitrogen source. Clamps were times costing still exhibited a continuous red color along the balloon, indicating that it did not wear off. Further examination for lubricity showed that the tubricity of the section of balloon given the above while applying firm linger pressure. After this, the abrasion test was the same as a similar section that was not rubbed.

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The integrity of the coeting after the abrasion test was further verified by allowing the coated tubing to dry and reexamining the coated surface under a 50x optical microscope. A continuous, unruptured coating was observed.

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Example 2

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A lubing measuring 0.017 in. in liner diameter and having an outer diameter of 0.0315 in. was coated and tormed into a balloon using the procedure of Example 1. When Inflated the balloon massured 0.100 in. in diameter along a central cylindrical section 0.740 in. long. There were conical approximately 0.165 in. at one end and tapering at the other end from 0.100 in. in diameter to 0.040 in. atong a length of approximately 0.165 in. at the other end. The wall thickness of the balloon in the sections at each end, tapering at one end from 0.100 in. In diameter to 0.034 in. along a length of center cylindrical portion-was about 0.001-in...

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Hammer and the process of forming the balloon, the costatement ed surface of the tubing underwent a radial expansion of 217% as well as an indeterminate amount

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ous coating of a crosslinked polyurethane poly-(ethylene oxide) complex. When viewed under 30 X optical microscope, a smooth coating was ob-served, free from fissuring, crazing or other sign of coating rupture. The coating continuity was further tion for 20 seconds, followed by insling in tap water to remove excess Congo Red. A continuous red film was observed, corresponding to the coatdisclosed by staining the coating, by immersing the coated balloon in 0.5% aqueous Congo Red solu-The surface of the balloon contained a continu-

ing, which absorbs the dye.

The wet coating on the baltoon exhibited a high degree of lubricity as determined by rubbing the coated baltoon between the lingers white applying a firm pressure, and comparing the base of movement to their observed when performing the same test on a similar wet balloon which did not contain a coating. The uncoated balloon, even when wel, offered significantly more resistance to movement than the coated balloon.

The durability of the coaling was determined by placing a coaled, stained balloon under a stream of running tap water and rubbing the coating between the finger and thumb for a total of 20 times while applying firm finger pressure Affer this. the coating still exhibited a continuous red color along the balloon, indicating that it did not wear off. Further examination for lubricity showed that the lubricity of the section of balloon given the above abrasion test was the same as a similar section

The integrity of the coating after abrasion test was further verified by allowing the balloon to dry, and reexamining the coated surface under a 30 X optical microscope. A continuous, unruptured coalthat was not rubbed.

The coaled belloon was then subjected to 10 cycles of wetting, tidricity testing, and dryling. It was found that the lubricity observed did not change even after 10 wetting and dryling cycles.

A coating formulation was prepared by weighing the following components into a disposable

1) 3.61 grams of CB-60 (the isocyanate de-

3) 150 grams of a 3.3 wt. % methylene chloride solution of Polyox WSR N-750

ponents were thoroughly mixed with a spatula to produce a uniform coating solution having total solids content of 2.25 vt. %. (ethylene oxide) described in Example 1); and 4) 283 grams of methylene chloride. The com-

lengths of polyethylene terephilhatate fubing measuring 0.050 in. by 1.0 in. and having an outer diameter of 0.082 in. were plugged at the bottom end by insertion of a short length of 0.050 in. seconds. The tubings were then air dried at ambient conditions for a period of between 15 minutes and 120 minutes and then baked 8 hours at 50 °C. The citing solution was then transferred to an 18 inch long glass tube having a 34 in. outler diameter which was plugged at one end. The glass tube was used as a dipping vessel. Twelve inch coating solution to a depth of 9.5 in. during 38 Tellon rod. The tubings were then dipped in the to effect cure of the coaling. Continuous coalings consisting of a crosslinked polyurethane complexed or associated with poly(ethylene oxide) were formed on the tubings. 15 8

then simultaneously pressurized and stretched for-gliudinally and radially to form the balloons. The balloons were then heated for about 30-40 seconds at about 300°F to crystallize the PET. The final balloons had a central cylindrical segment 1.10 in, long having an outer diameter of approximately 0.320 in, with a conical section at each end. One conical section tapered from 0.320 in, to 0.085 in, along a length of 0.75 in. The other conical section The tubings were then formed into a dilatation balloon using the stratching, heating, and blow molding methods disclosed in U.S. Re. 22,383 (to S.B. Levy). The tubings were heated at 180° F and in the central cylindrical portion was about 0.0015 In. in the process of forming the balloon, the coated surface of the tubing underwent a radial expansion of 290% as well as an indeterminate amount tapered from 0.320 in. to 0.100 in. along a length of 0.75 in. The wall thickness of the coated balloons 35 â 32 8

2) 2.78 grants of a saturated polyester polyol so having the same dimensions formed by the same (Multon R-12A, Miles Corporation) which typic call, has a hydroxyl contlant of 5%, equivalent call, has a hydroxyl contlant of 5%, equivalent ity issting. The ability of the coating the fubric call, has a hydroxyl contlant of 5%, equivalent ity issting. The ability of the coating the fubric value of 17.700 mPa's, and flash it ocycles of wetting, tubricity lesting, and drying myscosity @ 20°C of 17.700 mPa's, and flash point (Pensky-Marten closed up) of 320°F ss was also tested. The results were the same as There was a continuous coating on the surface of the balloon. The coated surface was viewed under a 30 X microscope and it was free from slippery when compared to an uncoated balloon fissuring, crazing or other signs of coaling rupture. The costed balloons were tested for lubricity using the procedure of Example 2 and found to be very those reported in Example 2. ş

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A coating formulation was prepared by weighing the following components into a disposable

- 1) 1.82 grams of CB-60 (the isocyante described in Example 1);
 - 2) 3.86 grams of the polyester resin Multron R-18 (the polyester/polyol described in Example
- 3) 150 grams of 3.3 wt. % methylene chloride solution of Polyox WSR N-750 (the poly-tethylene oxide) described in Example 1); and
- components were mixed thoroughly with a spatula to produce a uniform coating solution hav-4) 284 grams of methylene chloride. ing a total solids of 2.25 wt. %.. 홑

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tubing was air dried and cured using the conditions described in Example 3. The coating consisted of a crosslinked polyurethane complexed or associated The coating was applied to the polyethylene the same equipment and dip process. The coated terephthalate tubing described in Example 3 using with poly(ethylene oxide).

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balloon using the process described in Example 3. The tubing was then formed into a dilatation The balloon had the same dimensions.

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integrity after lubricity testing, and retained its lubricity after 10 cycles of wetting, lubricity testing, and drying as described in Example 2. wetled with water. The coaling exhibited durability, A continuous coating was observed on the balloon surface. The coating became slippery when

Example 5

A coating formulation was prepared by weighing the following components into a disposable

lecular weight (M_a,) of 124,000, and tensile @ break of 4000 psi and elongation at break of 750% at 1.5 Mil in MEK and tensile @ break of 3300 psi and elongation @ break of 760% at 1.5 15% total solids in cyclo hexanone; a Tg of 1) 115.7 grams of a 5 wt. % solution in methylene chloride of a thermoplastic polyesterurethane (Estane 5703F available from B.F. Goodrich Corp.) which has a Brookfield viscosity of 260 cps. at 15% total solids in methyl ethyl ketone (MEK) and of 1600 cps. at -20 · C (DSC/second heat), a weight average momil in cyclohexanone.

(Polyox WSR N-60K; Union Carbide Corp.); and components were thoroughly mixed with 3) 55.7 grams of methylene chloride.

spatula to produce a uniform coating solution having a total solids content of 2.25 vt. %. The coating was a blend of the polyurethane and the high ratio of the polyurethane to poly(ethylene oxide) molecular weight poly(ethylene oxide). The weigh

terephthalate tubing described in Example 2 using the same process. A dilatation balloon was blown The coating was applied to the polyethylene using the process described in Example 2. The

lubricity. However, the coating lost lubricity rapidly when rubbed with firm linger pressure under running water and became non-slippeny after 5 ruband found to still have continuous coating. Presumably this was the Estane which was not altered by exposure to water, other than by the loss of some bing cycles. This was probably due to leaching of some of the poly(eithylene oxide) into the water. After lubricity testing, the surface of the balloon the coated balloon exhibited a high degree of initlal was microscopically reexamined under 30 X power There was a continuous coating on the surface of the balloon, as indicated by microscopic examination under 30 X power. When wetted with water, of the admixed poly(ethylene oxide). balloon had the same dimensions.

Example 6

ing that the coating of Example 1 cannot be used This example is a comparative example show on a pre-formed polyurethane balloon.

in during 38 seconds as before. The balloon was air dried at ambient conditions for a period of about an hour and then baked 8 hours at 50°C to effect cure of the coating. The result was an adherent cure of the coating. the same dimensions as the balloon described in Example 3. The balloon end of the catheter was dipped into the coating solution to a depth of 9.5 coating which exhibited good lubricity and durability when wetled with water. However, there was The coating solution described in Example 3 ethylene terephthalate tubing as before, the coating was applied in a conventional manner. The distall end of a catheter shaft contained a pre-formed, significant axial shrinkage in the balloon which caused the catheter shaft to buckle in the region This rendered the catheter useless as a medical was prepared. Instead of coating a length of polyinflated polyethylene terephthalate balloon having between the two adhesively bonded balloon ends. 33 \$ ş 20

A coating formulation was prepared weighing 4.0 grams of a thermoplastic hydrophilic polyurethane polymer, available as D-6/40 from Tyndale

Plains-Hunter, Ltd., Ringoes, NJ into an eight ounce glass bottle. A total of 196 grams of methylene chloride was then weighted into the overnight to produce a uniform solution containing bottle, which was subsequently capped and rolled 2 wt. % of the polymer.

Twetve inch lengths of the polyethylene terephthale tubing described in Example 3 were dip coated in this solution by immersing them at about at ambient conditions for a period of 20-30 minutes and then baked at 100 °C for twenty minutes. The inches per second. The coated tubes were air dried tubes were then formed into a dilatation balloons as described in Example 3. The resulting dimensions then withdrawing them at a speed of about 0.25 inch per second to a depth of about 9 inches and expansion were as described therein.

2 25 gers. Lubricity was not diminished after twenty cycles of rubbing. The coating was stained in 0.5% aqueous Congo Red solution and it was found to over their entire surface. When viewed under a 30 X microscope the surface was observed to be free of fissuring, crazing or other sign of coaling rup-ture. The balloon surface was wetted with water and found to be more lubricous than a similar The balloons exhibited a continuous coating uncoated balloon when rubbed between the finbe continuous and hydrophilic.

Example 8

\$ polyfunctional aziridine crosslinker (available as KM10-1703 from Stahl Incorporated, Peabody, MA) into an 8 ounce glass bottle. A total of 195 grams dimethylsiloxane slip agent (available as UE-41-568 form Stahl Incorporated) was then weighed into the mulation was prepared by weighing 5.0 grams of a of a polyurethane emulsion containing a polybottle which was subsequently capped and rolled A non-hydrophilic protective slip-coating for-30 minutes to produce a uniform dispersion.

Ş 20 Twelve inch lengths of the polyethylene tereph-thatate tubing described in Example 3 were dip coated as described in Example 7. The tubings were allowed to air dry at ambient conditions for a polyurethane. The tubings were then formed into dilatetion balloons as described in Example 3. The baked at 51°C for 20 minutes to crosslink the period of at least 5 minutes. Then the tubings were resulting dimensions and expansion were as described therein.

cover_their_enlire_surface_as_evidenced_by_micro-scopic examination at 30 X. The dry balloon sur-The balloons exhibited a continuous coating face, which contained a significant amount of polydimethyl siloxane slip agent, was observed, when rubbed between the fingers, to feel slippery in

comparison to a similar uncoated balloon.

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readily apparent to those skilled in the art. Accordingly, the spirit and scope of the present invention are to be limited only by the appended claims and lications and improvements thereon will become that the preferred embodiments of the invention have been given in detail, various modinot by the foregoing specification. Now

Claims

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- A process for preparing a coated expanded thermoplastic medical product, which comprises the steps of:
 - (a) applying to at least a portion of an inner and/or an outer surface of an expandable thermoplastic tubing at least one adherent prises at least one biomedical functional functional biomedical coating which comagent and a carrier,

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- time and temperature sufficient to remove at least part of the carrier; and (c) stretching and/or expanding the dried (b) allowing the coated tubing to dry at a
 - coated tubing with an inflating fluid at a pressure sufficient to form the coaled expanded medical product.
- The process of Claim 1, further comprising the step of healing the partially dried coated tubing at a temperature and for a time sufficient to soften the coated tubing prior to stretching and/or expansion. d

- ylene-butylene-styrene block copolymers admixed with low molecular weight styrene and The process of Claim 1, wherein the tubing is ylene; polypropylene; polyethylene tereph-thelate; polybutylene terephthalate; polyvinyl optionally propylene; and polyether polyamide block copolymers and wherein the coating is a selected from the group consisting of polyethpolyamides; polyamideimides; polycarbonates; ionomers; polyaryl ether ketones; polyurethane; ethylene-vinyl acetate copolymers; ethpolyetherimides polyimides; ubricious coating. chloride; લ
- is polyurethane or polyethylene terephthalate and wherein the coating contains a poly-The process of Claim 3, wherein the substrate (ethylene oxide), a polyvinyl pyrrolidane, a hydrophilic polyurethane, or a silicone.
- 5. The process of Claim 4, wherein the coaling polymer selected from the group consisting of contains poly(ethylene oxide) a preformed polyurethane, a polyurea, and a polyurethane-urea or contains polymer precursors se-

- The process according to Claim 5, wherein the coating comprises a crosslinked polyurethane
- The uniformly functionally coated expanded thermoplastic medical product prepared by the process of Claim 1.

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- The uniformly functionally coated expanded themoplastic medical product prepared by the process of Claim 3.
- The uniformly functionally coated expanded thermoplastic medical product prepared by the process of Claim 4.
- The uniformly functionally coated expanded thermoplastic medical product prepared by the process of Claim 5.

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11. The uniformly functionally coaled expanded thermoplastic medical product prepared by the process of Claim 6.

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- (a) applying to at least a portion of an inner and/or an outer surface of an expandable A process for preparing a coated balloon, which comprises the steps of: thermoplastic tubing at least one adherent tubricious coating which comprises at least Ճ
- (b) altowing the coated tubing to dry at a time and temperature sufficient to remove at one fubricious agent and a carrier;

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least part of the cerrier; and
(c) stretching and/or expanding the dried coated tubing with an inflating fluid at a pressure sufficient to form the coated bal-

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The process of Claim 12, further comprising the step of heating the partially dried coated tubing at a temperature and for a time sufficient to soften the coated lubing prior to stretching and/or expansion. Ę

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choride; — polyimides; — polyatherimides; — polyamides; polyamidelmides; polyacarbonatés; Eparkerases innomers; polyaryl ether kelones; polyure ss 20 thatate; polybutytene terephthalate; polyvinyl The process of Claim 12, wherein the tubing is selected from the group consisting of polyethy ylene-butylene-styrene block copolymers admixed with low molecular weight styrene and thane; ethylene-vinyl acetate copolymers; ethž ١:

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- optionally propylene; and polyether polyamide block copolymers and wherein the coating is a lubricious coating.
- The process of Claim 12, wherein the substrate is a polyurethane or polyethylene terephthate and wherein the coating is a lubricious coaling comprising a hydrophilic polyurethane and an organic solvent. ξį
- tective tubrictious coaling compulsing an aqueous dispersion of a urethane, a silicone or siloxane emulsion, and optionally a polyfuncstrate is a polyurethane or polyethylene terephthatate and wherein the coating is a pro-The process of Claim 12, wherein the subtional aziridine as a crosslinking agent.

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- strate is a polyurethane or polyethylene terephthalate and coating contains poly-(ethylene oxide) and a preformed polymer selected from the group consisting of a polyurethane, a polyurea, and a polyurethane-urea or contains polymer precursors selected from the 17. The process of Claim 12, wherein the subgroup consisting of polyurethane precursors and polyurea precursors.
- The process according to Claim 12, whereIn the coating comprises a crosslinked polyure-. ₩

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- The coated balloon prepared by the process of €
- A process for preparing a lubricious dilatation balloon, which comprises the steps of:

 (a) applying to at least a portion of an outer surface of a thermoplastic tubing at least one adherent tubricious coating which comprises (i) a carrier, (ii) a poly(eithylene oxide) dissolved, dispersed, or emulsitied in the carrier, and (iii) a polymer selected from the group consisting of a polyurethane, a mer precursors selected from the group polyurea, and a polyurethane-urea or polyconsisting of polyurethane precursors and polyurea precursors, the polymer or polymer precursors being dissolved, dispersed. 20.
- (b) allowing the coated tubing to dry at a time and temperature sufficient to remove at or emulsified in the carrier;
- least part of the carrier; and (c) expanding the dried coated tubing with an initiating fluid in order to increase the diameter and tength of the tubing white simultaneously orienting the tubing and forning the tubricious dilatation balloon.

 The process of Claim 20, wherein the orienting step includes heating the coated tubing to a the second order transition temperature to the temperature within the range extending from first order transition temperature of the thermoplastic polymer.

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expanding the drawn oriented section to a modified profile and size, further followed by heat setting the modified profile and size to The process of Claim 21, further comprising the step of drawing the oriented section to provide a drawn oriented section, followed by form the coated balloon. 22

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The process of Claim 20, wherein the tubing is selected from group consisting of polyethylene; polypropylene; polypropylene; polypropylene terephithalate; polybutylene terephithalate; polybutylene chloride; polyimides; polyetherimides; polyamides; polyamides; polycarbonales; ionomers; polyaryl ether kelones; polyureylene-butylene-styrene block copolymers admixed with low molecular weight styrene and optionally propylene: and polyether polyamide thane; ethylene-vinyl acetate copolymers; eth-ដូ

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The process of Claim 23, wherein the tubing is polyethylene terephthalate. 4

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- The process of Claim 23, wherein the tubing is ķ
- 26. The process of Claim 23, wherein the tubing is a segmented polyurethane.
- The process of Claim 23, wherein the segmented polyurethane contains at least 45 wt.% of soft segments with the balance being hard 27.

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- Ş The process of Claim 23, wherein the carrier is selected from the group consisting of water, methylene chloride, methylene bromide, trich toroethylene, ethylene dichloride, N-methylpyrrolldone, pyridine, and mixtures thereof. , 28
- S 29. The process of Claim 23, wherein the polymer is polyurethane or polyurethane-urea which is prepared from a diisocyanele, a polyether glycol, and a chain extender.
 - The process of Claim 29, wherein the chain extender is selected from the group consisting of water, a low molecular weight diol, a diisocyanate is methylene diisocyanate, the polyether glycol is polyethylene glycol, and the ģ

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- or an amino alcohol of up to carbon atoms, and mixtures thereof.
- is an intimate physical mixture of about 50-98% by weight of a polyurethane and about 2-50% by weight of a poly(ethylene oxide) having a molecular weight of at least 10,000 in a 31. The process of Claim 23, wherein the coaling
- 32. The process of Claim 31, wherein the polyure-thane is a alliphatic polyurethane and the car-
- 33. The process of Claim 23, wherein the coating is a crosslinked polyurethane matrix associated or complexed with a poly(ethylene oxide).
- thane matrix is prepared by coating the tubing with a solution consisting essentially of an isocyanate, a polyol, and the polyethylene oxide dissolved in a sulfable solvent. 34. The process of Claim 33, wherein the polyure-
- polyester polyols, polyacrylate polyols; wherein the poly(ethylene oxide) has a molecular weight of about 10,000-5,000,000 and wherein ing of solvents methylene chloride. loroethylene, pyridine, n-methyle pyrrolidone, dioxolane, acetonitrile, and blends of the ing of 2,4- and 2,6-toluene disocyante and disocyante and prepolymers thereof, diphenyl-methane 4,4-disocyante and prepolymers the polyol is selected from the group consisting of polyol selected from the group of cestor the solvent is selected from the group consist-The process of Claim 32, wherein the isocyanate is selected from the group consistthereof, bis(4-tsocyanatocyclohexyt) methane diisocyante and prepolymers thereof, wherein oil and castor oil derivatives, saturated polyester polyols, polyether polyols, unsaturated dichloroethylene, trichand prepolymers thereof, and isophorone thereof. dibromomethane, prepolymers 33

- The lubricious dilatation balloon prepared by the process of Claim 20. 36.
- an abrasion resistant hydrophilic hubricous coaling Which is a continuous film of a cross-manager stinked substantially polyurethane matrix comthe process of Claim 36, wherein the coating is The lubricious dilatation balloon produced by plexed or associated with a poly(ethylene ox-ide). 37.

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Suropean Patent Office

EUROPEAN SEARCH REPORT

Application Number EP 93 11 5730

| _ | | DOCUMENTS CONSIDERED TO BE RELEVANT | | | _ |
|--------|---------------|--|----------------------|--|-----|
| | Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | AFFLICATION (I-LCLS) | |
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| | > | EP-A-D 454 293 (C.R. BARD, INC.) * column 3, line 28 - column 6, line 48; | 1-38 | | |
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